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## PAPER

# Photophysical and electrochemical properties of Ru(II) complexes containing tridentate bisphosphino-oligothiophene ligands<sup>†</sup>

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Nine Ru(II) complexes containing the conjugated oligothiophene ligands 3,3''-bis(diphenylphosphino)-2,2':5',2''-terthiophene (P<sub>2</sub>T<sub>3</sub>) and 4',3'''-bis(diphenylphosphino)-3,3''''-dihexyl-

2,2':5',2'':5'',2''':5''',2''''-pentathiophene ( $P_2T_5$ ) were prepared and characterized.  $P_2T_3$  and  $P_2T_5$  bond as tridentate ligands and three of the complexes (1, 2 and 5) form green five-coordinate Ru(II) complexes in solution. Cyclic voltammetry, variable temperature UV-vis spectroscopy and time-resolved transient absorption spectroscopy were used to characterize the electronic properties of the complexes. Increased conjugation in the complexes containing the  $P_2T_5$  ligand resulted in a lowering of the oxidation potential of the oligothiophene, but electropolymerization was not observed. The electronic spectra were dominated by  $\pi$ - $\pi$ \* transitions. All of the complexes were non-emissive both at room temperature and low temperature, indicating the excited state decays by other, non-radiative pathways. The transient absorption spectrum of complex 7 shows a species with a band at 475 nm and a lifetime of ~100 ns, assigned to a ligand-based triplet state.

#### Introduction

Photoelectrochemical cells using Ru(II) dyes for light harvesting have drawn significant attention.<sup>1-7</sup> These cells typically utilize photogenerated charge transfer states at the metal to inject electrons into a wide band gap semiconductor such as TiO2.1,8 Ru(II) complexes with polypyridyl ligands are of particular interest since their photophysical properties, photochemical reactivity and electrochemical characteristics are all suitable for application in photoelectrochemical cells. The most efficient Grätzel-type cells use N719 or Black dye, both of which result in efficiencies of > 10%.<sup>9,10</sup> Alternate approaches to light harvesting utilize conjugated polymers<sup>11-16</sup> or molecules/oligomers<sup>12,13,17-19</sup> to absorb light and separate charge. Polymer blends such as P3HT/PCBM (P3HT = poly-3-hexylthiophene, PCBM = 1-(3-methoxycarbonyl)propyl-1phenyl-[6,6]-methanofullerene) offer the possibility of enhanced electron-hole separation by electron transfer from a P3HT excitons to PCBM.<sup>20</sup> Devices using conjugated materials are projected to reach comparable efficiencies to Ru(II)-based devices.<sup>21</sup>

A hybrid approach to light harvesting involves using oligoor polythiophenes as ligands on Ru(II). Solid-state cells in which Ru(II) dyes have been doped into poly-3-octylthiophene and poly(3,4-ethylenedioxythiophene) films show efficiencies of  $0.16\%^{22}$  and  $2\%^{23}$ , respectively. Thiophenes have also been appended to ligands in Ru(II)-bipyridine complexes<sup>24–27</sup> and used in dye-sensitized solar cells with reported efficiencies of  $\sim 6\%^{25} - \sim 9\%$ .<sup>26,27</sup> These results suggest that Ru(II) complexes in which thiophene-based ligands are closely coupled to the metal centre may be good candidates as dyes for photoelectrochemical cells.

Our group has previously investigated several Ru(II)-bpy complexes with oligothiophene ligands.<sup>28,29</sup> These complexes have been shown to exhibit long-lived charge-separated states,<sup>30</sup> and broad light absorption across the visible spectrum. One problem that was encountered with many of these complexes is twisting in the oligothiophene backbone when the metal is bound. This results in disruption of conjugation along the backbone and consequently loss of the electronic delocalization necessary for effective charge separation in the ligand. In order to overcome this weakness we designed a new bisphosphine ligand,  $P_2T_3$ ,<sup>31</sup> in which a central, unsubstituted thiophene is flanked by two diphenylphosphino substituted rings. Coordination of a metal to this ligand is possible without extensive backbone twisting, moreover tridentate coordination is possible if the central sulfur also coordinates in addition to the two phosphines. We have shown that  $P_2T_3$  can coordinate to Au(I), and were interested in examining binding of this ligand to Ru(II) with a variety of other ancillary ligands surrounding the metal. In this paper, we report a series of new neutral and cationic Ru(II) complexes containing the  $P_2T_3$  ligand (Scheme 1), along with the electrochemical and photophysical properties of these complexes. In addition, P2T5, a more conjugated analog of  $P_2T_3$  is reported along with two complexes containing this new ligand, in order to explore the effect of conjugation length on the properties of the complexes.

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#### Experimental

#### General

 $P_2T_3$ <sup>31</sup>  $Br_2T_3$ <sup>32</sup> and 2-(3-hexyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane<sup>33</sup> were prepared by literature procedures. PPh<sub>2</sub>Cl was purchased from Strem; 2-bromothiophene, 3hexylthiophene, and N-iodosuccinimide (NIS) from Sigma Aldrich; trimethylsilyl-acetylene from Acros; and n-Bu<sub>4</sub>NF from Fluka Chemicals. Diethyl ether (Et<sub>2</sub>O) and tetrahydrofuran (THF) were dried over Na/benzophenone. CH2Cl2 was dried over an activated alumina column. Acetonitrile was dried over 3 Å sieves. All other solvents were used as received. Ru(DMSO)<sub>4</sub>Cl<sub>2</sub>,<sup>34</sup> Ru(2,2'-bpy)Cl<sub>2</sub>(DMSO)<sub>2</sub>,<sup>35</sup> and Ru(tpy)Cl<sub>2</sub>(DMSO)<sup>36</sup> were prepared according to literature procedures. Ruthenium(III) chloride hydrate was purchased from Strem. NMR spectra were obtained on either a Bruker AV-300 or Bruker AV-400 spectrometer and referenced to residual solvent or external H<sub>3</sub>PO<sub>4</sub>. UV-vis spectra were obtained on a Varian-Cary 5000 UV-vis-near-IR spectrophotometer in HPLC grade CH<sub>2</sub>Cl<sub>2</sub> or acetonitrile. Infrared spectra were obtained on a Nicolet 6700 FTIR with a Smart Orbit<sup>TM</sup> accessory. Low temperature absorption and emission spectra were obtained using an Oxford OptistatDN cryostat using solutions of EtOH:MeOH (4:1) with DMF as needed (to dissolve 1-4). Transient absorption measurements were carried out on a Princeton Instruments Spectra Pro 2300i Imaging Triple Grating Monochromator/Spectrograph with a Hamamatsu Dynamic Range Streak Camera (excitation source: EKSPLA Nd:YAG laser,  $\lambda = 355$  nm) with aerated and deaerated solutions. Cyclic voltammetry data were obtained on an Autolab potentiostat with a platinum disk working electrode, silver wire reference electrode, and platinum mesh counter electrode. Decamethylferrocene was used to correct the potentials to saturated calomel electrode (SCE). The electrolyte was  $[n-Bu_4N][PF_6]$ , which was recrystallized three times from ethanol and heated to 90 °C under vacuum for three days prior to use.

#### Synthetic Procedures

3,3"-Dibromo-5,5"-diiodo-2,2':5',2"-terthiophene ( $I_2Br_2T_3$ ). Br<sub>2</sub>T<sub>3</sub> (1.00 g, 2.46 mmol) was dissolved in a mixture of AcOH (42 mL) and CHCl<sub>3</sub> (83 mL) in the dark. NIS (1.11 g, 4.92 mmol) was added and the mixture stirred overnight. The CHCl<sub>3</sub> was removed *in vacuo*, and a yellow solid precipitated. The precipitate was vacuum filtered, and rinsed 3 times with water, 3 times with MeOH, and once with Et<sub>2</sub>O to obtain I<sub>2</sub>Br<sub>2</sub>T<sub>3</sub>. Yield: 1.02 g, 63%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>);  $\delta$  7.30 (s, 2H), 7.17 (s, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  140.5, 137.5, 134.0, 126.8, 107.9, 72.17. EI-MS *m/z* 658 (100%, [M]<sup>+</sup>). Anal. Calcd for C<sub>12</sub>H<sub>4</sub>Br<sub>2</sub>I<sub>2</sub>S<sub>3</sub>: C, 21.90; H, 0.61. Found: C, 22.07; H, 1.02.

4',3'''-Dibromo-3,3''''-dihexyl-2,2':5',2'':5'',2''':5''',2''''-pentathiophene (Br<sub>2</sub>T<sub>5</sub>). I<sub>2</sub>Br<sub>2</sub>T<sub>3</sub> (700 mg, 1.06 mmol), 2-(3-hexyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (680 mg, 2.30 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (133 mg, 0.11 mmol) were dissolved in N<sub>2(g)</sub> sparged THF (100 mL). A NaHCO<sub>3</sub> solution (18 mL, 0.4 M) was added to the THF solution. The mixture was heated to reflux and stirred overnight. The THF was removed in vacuo and the remaining water was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The CH<sub>2</sub>Cl<sub>2</sub> was dried with MgSO<sub>4</sub>, filtered and the CH<sub>2</sub>Cl<sub>2</sub> was removed in vacuo. The residue was purified via column chromatography on silica using hexanes as the eluent.  $Br_2T_5$  was collected as an orange oil. Yield: 681 mg, 87%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>); δ 7.42 (s, 2H), 7.23 (d, 2H, J = 5.2 Hz), 7.04 (s, 2H), 6.96 (d, 2H, J = 5.2 Hz), 2.78 (t, 4H, J = 7.8 Hz), 1.67 (m, 4H), 1.34 (m, 15H), 0.92 (m, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 141, 135.3, 135.6, 131, 130.1, 129.8, 129, 126, 125, 108, 32, 31, 30, 29, 23, 14. EI-MS m/z 738 (60%, [M]<sup>+</sup>), 572 (100%, [M - C<sub>6</sub>H<sub>13</sub> - Br - 2H]<sup>+</sup>). Anal. Calcd for C<sub>32</sub>H<sub>34</sub>Br<sub>2</sub>S<sub>5</sub>: C, 52.03; H, 4.64. Found: C, 52.36; H, 4.76.

4',3'''-Bis(diphenylphosphino)-3,3''''-dihexyl-2,2':5',2'':5'',2''': 5<sup>'''</sup>,2<sup>''''</sup>-pentathiophene ( $P_2T_5$ ). Br<sub>2</sub>T<sub>5</sub> (812 mg, 1.11 mmol) was dissolved in diethyl ether (50 mL) and cooled to -78 °C. n-BuLi in hexanes (1.74 mL, 2.78 mmol) was added to the bright yellow solution. The solution immediately changed to dark red in colour. Gradually, it was warmed to -30 °C and Ph<sub>2</sub>PCl (0.52 mL, 2.89 mmol) was added. The solution was warmed to room temperature overnight. The solution was then quenched with 50 mL of water. The ether layer was removed in vacuo and the water was decanted. The remaining residue was rinsed three times with water (~ 50 mL). The residue was dissolved in minimal acetone and then sonicated with MeOH (~ 20 mL) resulting in a bright orange oily residue at the bottom in the flask. The orange oil was then left under vacuum overnight, giving orange  $P_2T_5$  powder. Yield: 316 mg, 30%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>); δ 7.36 (m, 20H), 7.13 (d, 2H, J = 5.1 Hz), 7.10 (s, 2H), 6.88 (d, 2H, J = 5.1 Hz), 6.57 (s, 2 Hz), 2.58 (t, 4H, J = 7.8 Hz), 1.25 (m, 16H), 0.89 (m, 6H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>)  $\delta$  –23.8 ppm. EI-MS *m*/*z* 946  $(40\%, [M]^+)$ , 930 (90%,  $[M - CH_3]^+$ ), 780 (90%,  $[M - C_{12}H_{26}]^+$ ), 764 (100%, [M-PPh<sub>2</sub>]<sup>+</sup>). Anal. Calcd for C<sub>56</sub>H<sub>54</sub>P<sub>2</sub>S<sub>5</sub>: C, 70.85; H, 5.73. Found: C, 70.98; H, 5.50.

Complex 1. Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (78.6 mg, 0.162 mmol) and  $P_2T_3$  (100 mg, 0.162 mmol) were added to degassed toluene (3 mL). The yellow slurry was heated to reflux for two hours, during which time it gradually became red and an orange precipitate formed. The solution was cooled to room temperature and the orange precipitate was vacuum filtered. Yield: 93 mg, 64%. <sup>1</sup>H NMR

(300 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 (m, 4H), 7.69 (m, 4H), 7.44 (s, 2H), 6.96 (d, 2H, J = 5.4 Hz), 1.79 (s, 6H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>)  $\delta$  1.5 (s). Anal. Calcd for (C<sub>38</sub>H<sub>32</sub>Cl<sub>2</sub>OP<sub>2</sub>RuS<sub>4</sub>)·2(H<sub>2</sub>O): C, 50.55; H, 4.02. Found: C, 50.46; H, 4.06. IR 1007.0 cm<sup>-1</sup> (v(S=O)).

Complex **2**. A slurry of Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (393 mg, 0.811 mmol) and P<sub>2</sub>T<sub>3</sub> (500 mg, 0.811 mmol) in toluene (15 mL) was heated to reflux. Gradually, the two solids dissolved to form a dark red solution, and subsequently an orange solid precipitated. After two hours, the solid was vacuum filtered and dissolved in minimal hot DMF/acetonitrile solution (1:1, ~10 mL). Ether (10 mL) was added to the solution and it was cooled to 4°C overnight. A dark red precipitate formed and was vacuum filtered. Yield: 400 mg, 73%. Crystals suitable for x-ray diffraction were grown from an acetonitrile/DMF/ether solution. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.16 (m, 4H), 7.49 (m, 4H), 7.44 (s, 2H), 7.34 (m, 14H), 6.97 (d, 2H, J = 5.2 Hz), 1.11 (s, 3H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.7 (s). ESI-MS *m*/*z* 753 ([M-CH<sub>3</sub>CN-Cl]<sup>+</sup>). Anal. Calcd for (C<sub>38</sub>H<sub>29</sub>Cl<sub>2</sub>NP<sub>2</sub>RuS<sub>3</sub>)·(C<sub>3</sub>H<sub>7</sub>NO): C, 54.54; H, 4.02; N, 3.10. Found: C, 54.85; H, 4.08; N, 3.16.

Complex **3**. A slurry of **2** (100 mg, 0.11 mmol) and 4,4'bpy·2H<sub>2</sub>O (50 mg, 0.26 mmol) in acetone (20 mL) was heated to reflux for four hours. The solution was cooled and filtered through neutral alumina resulting in a green solution. The solution was concentrated, and the resulting precipitate vacuum filtered. Yield: 20 mg, 19% yield. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.74 (m, 1H), 8.65 (m, 1H), 8.49 (d, 1H, J = 6.3 Hz), 8.14 (m, 4H), 7.88 (d, 2H, J = 6.3 Hz), 7.63 (d, 1H, J = 5.4 Hz), 7.54 (s, 2H), 7.35 (m, 8H), 7.22 (d, 1H, J = 5.4 Hz), 7.03 (m, 2H), 6.94 (m, 4H), 6.85 (m, 6H), 6.38 (m, 1H), 6.35 (m, 1H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz)  $\delta$  8.3 (s). ESI-MS *m/z* 909 ([M-Cl]<sup>+</sup>). Anal. Calcd for (C<sub>47</sub>H<sub>36</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>RuS<sub>3</sub>)·2H<sub>2</sub>O: C, 56.32; H, 3.90; N, 2.86. Found: C, 56.17; H, 3.86; N, 2.89.

Complex 4. In a 50 mL round bottom flask, 2 (100 mg, 0.11 mmol) and N-Me-4,4'-bipyridinium iodide (33 mg, 0.11 mmol) were ground together to make a homogeneous mixture. The mixture was then heated to 100°C under nitrogen. A vapor of CH<sub>3</sub>CN condensed around the top of the round bottom flask during the two hours that it was heated. The mixture was cooled overnight, then dissolved in CHCl<sub>3</sub> and filtered. The solution was evaporated, leaving a brown solid. Yield: 106 mg, 88%. <sup>1</sup>H NMR  $(CDCl_3, 400 \text{ MHz}) \delta 9.19 \text{ (m, 2H)}, 8.80 \text{ (d, 2H, J} = 4.4 \text{ Hz}), 8.10$ (m, 2H), 8.02 (quart, 4H, J = 5.7 Hz), 7.64 (m, 4H), 7.60 (m, 2H), 7.46 (s, 2H), 7.42 (m, 1H), 7.35 (m, 5H), 7.28 (d, 2H, J = 5.2 Hz), 7.20 (m, 1H), 7.14 (t, 2H, J = 7 Hz), 7.07 (t, 3H, J = 7.2 Hz), 6.90 (d, 2H, J = 5.2 Hz), 4.22 (s, 3H).  ${}^{31}P{}^{1}H{}$  NMR (162 MHz)  $\delta$  7.4 (s). ESI-MS m/z 959 ([M-I]<sup>+</sup>). Anal. Calcd for (C<sub>47</sub>H<sub>37</sub>Cl<sub>2</sub>IN<sub>2</sub>P<sub>2</sub>RuS<sub>3</sub>)·H<sub>2</sub>O: C, 51.09; H, 3.56; N, 2.54. Found: C, 51.38; H, 4.01; N, 2.67.

Complex 5. Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (51.0 mg, 0.105 mmol) and P<sub>2</sub>T<sub>5</sub> (100 mg, 0.105 mmol) were added to N<sub>2(g)</sub> sparged toluene (3 mL). The mixture was heated to reflux for 2 hours. The toluene was removed *in vacuo*, the residue dissolved in CHCl<sub>3</sub> and the CHCl<sub>3</sub> solution was added to Et<sub>2</sub>O to precipitate a red powder. The slurry was centrifuged and the precipitate was rinsed 3 times with 10 mL of Et<sub>2</sub>O. Yield: 40 mg, 30%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 (m, 2H), 7.75 (m, 4H), 7.43 (s, 2H), 7.38 (m, 8H), 7.21 (m, 8H), 6.92 (d, J = 5.4 Hz, 2H), 6.89 (s, 2H), 2.59 (m, partially overlaps with free DMSO), 1.84 (s, overlaps with alkyl chain protons), 1.80 (m, overlaps with bound DMSO peak), 1.50 (m, 5H), 0.84 (t, 6H,

 $J = 6.6 \text{ Hz}). {}^{31}P{}^{1}H{} \text{ NMR (121 MHz) } \delta 1.9 \text{ (s). ESI-MS: } m/z 1087 \text{ ([M-Cl-DMSO]}^{+}). Anal. Calcd for C_{58}H_{60}Cl_2OP_2RuS_6 \cdot CH_3Cl: C, 53.73; H, 4.66. Found: C, 53.27; H, 4.62. IR 1015.0 cm^{-1} (v(S=0)).$ 

Complex 6. Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (39 mg, 0.081 mmol), AgBF<sub>4</sub> (33 mg, 0.17 mmol) and  $P_2T_3$  (100 mg, 0.16 mmol) were dissolved in acetonitrile (100 mL) and heated to reflux overnight. The solution was cooled to room temperature and then filtered through Celite. The Celite was rinsed with acetone and the filtrate evaporated until approximately 10 mL of solvent remained. The reduced filtrate was then filtered through glass wool and added to a solution of NH<sub>4</sub>PF<sub>6</sub> in water. Immediately, a vellow precipitate was observed, and after thirty minutes the precipitate was vacuum filtered. The yellow precipitate was then recrystallized in CHCl<sub>3</sub> and vacuum filtered. Yield: 10 mg, 13%. <sup>1</sup>H NMR (300 MHz,  $(CD_3)_2CO) \delta$  7.85 (d, J = 5.4 Hz, 2H), 7.78 (s, 2H), 7.70 (m, 6H), 7.50 (m, 14H), 7.01 (d, J = 5.4 Hz, 2H), 2.77 (s, 6H).  ${}^{31}P{}^{1}H{}$ NMR (121 MHz)  $\delta$  8.0 (s), -141 (sept). MALDI-TOF: *m*/*z* 835  $([M-PF_6]^+)$ . Anal. Calcd for C<sub>40</sub>H<sub>32</sub>ClN<sub>2</sub>P<sub>3</sub>RuS<sub>3</sub>F<sub>6</sub>: C, 49.01; H, 3.29; N, 2.86. Found: C, 48.65; H, 3.37; N, 2.58. IR 2283.9 cm<sup>-1</sup>  $(v(C \equiv N)).$ 

Complex 7. Ru(2,2'-bpy)Cl<sub>2</sub>(DMSO)<sub>2</sub> (485 mg, 1.00 mmol), AgBF<sub>4</sub> (214 mg, 1.10 mmol) and  $P_2T_3$  (617 mg, 1.00 mmol) in a CHCl<sub>3</sub> solution (300 mL) were heated to reflux overnight. The reaction was then cooled to room temperature, filtered through Celite, and the Celite washed with CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was evaporated and the residue dissolved in a minimal amount of acetone. The acetone was added to an aqueous solution of  $NH_4PF_6$ , resulting in an immediate orange precipitate. The mixture was stirred for one hour and the precipitate was vacuum filtered. The precipitate was purified by chromatography on neutral alumina, using first CH<sub>2</sub>Cl<sub>2</sub>, followed by acetone. Yield: 326 mg, 31%. Crystals suitable for single crystal x-ray diffraction were grown from acetone/MeOH/hexanes. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ):  $\delta$  9.12 (d, 1H, J = 5.6 Hz), 8.02 (d, 1H, J = 8 Hz), 7.87 (t, 1H, J = 7.6), 7.79 (d, 1H, J = 8.4 Hz), 7.77 (d, 1H, J = 5.6 Hz), 7.61 (t, 1H, J = 8 Hz), 7.56 (s, 2H), 7.46 (m, 5H), 7.30 (m, 4H), 7.24 (d, 2H, J = 7.2 Hz), 7.15 (t, 4H, J = 7.2 Hz), 6.82 (t, 4H, J = 8 Hz), 6.63 (d, 2H, J = 5.2 Hz), 6.59 (t, 1H, J = 6 Hz), 6.20 (m, 4H).<sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  9.5 (s), -141.8 (sept, J = 712 Hz). ESI-MS m/z 909 ([M-PF<sub>6</sub>]<sup>+</sup>). Anal. Calcd for C<sub>46</sub>H<sub>34</sub>ClF<sub>6</sub>N<sub>2</sub>P<sub>3</sub>RuS<sub>3</sub>: C, 52.40; H, 3.25; N, 2.66. Found: C, 52.57; H, 3.41; N, 2.62.

Complex 8. Ru(tpy)Cl<sub>2</sub>(DMSO) (78 mg, 0.16 mmol) and AgBF<sub>4</sub> (197 mg, 0.32 mmol) were dissolved in methanol (30 mL) and heated to reflux for nine hours. The solution was cooled to room temperature, filtered, and the filtrate added to a suspension of  $P_2T_3$ (100 mg, 0.16 mmol) in MeOH (30 mL). The mixture was heated to reflux and stirred overnight. The solution was then cooled to room temperature and added to a water solution (50 mL) containing NH<sub>4</sub>PF<sub>6</sub> (130 mg, 0.798 mmol). Immediately, an orange solid precipitated. The precipitate was stirred for one hour and the product was isolated by vacuum filteration. Yield: 102 mg, 51%. Crystals suitable for x-ray diffraction were grown from slow evaporation of a hexanes/acetone solution. 400 MHz <sup>1</sup>H NMR (d<sub>6</sub>-acetone)  $\delta$  8.46 (s, 3H), 8.21 (s, 2H), 7.90 (m, 4H), 7.78 (m, 4H), 7.26 (m, 6H), 7.02 (m, 8H), 6.65 (m, 10H). 161 MHz <sup>31</sup>P{<sup>1</sup>H} NMR  $\delta$  9.7 (s), -141.8 (sept, J = 702 Hz). EI-MS: m/z 1096 ([M- $(PF_6)^+$ , 475 ([M-(PF\_6)\_2]^{2+}). Anal. Calcd for  $C_{51}H_{37}F_{12}N_3P_4RuS_3$ : C, 49.36; H, 3.01; N, 3.39%. Found: C, 49.4; H, 3.31; N, 2.97.

Complex 9. Ru(tpy)Cl<sub>2</sub>(DMSO) (86 mg, 0.18 mmol) and AgBF<sub>4</sub> (73 mg, 0.37 mmol) were added to methanol (50 mL) and the solution heated to reflux for 15 hours. The solution was cooled to room temperature and filtered into a round bottom containing  $P_2T_5$  (169 mg, 0.178 mmol). The solution was heated to reflux for 24 hours and cooled to room temperature. The MeOH solution was added to a solution of  $NH_4PF_6$  (290 mg) in water and an orange precipitate immediately appeared. The orange precipitate was vacuum filtered to obtain the crude product (156 mg). The product was crystallized from MeOH/hexanes. Yield: 20 mg, 7.1%. <sup>1</sup>H NMR (d<sub>6</sub>-acetone, 400 MHz)  $\delta$  8.47 (s, 3H), 8.24 (s, 2H), 7.98 (d, 2H, J = 5.9 Hz), 7.91 (d, 2H, J = 7.8 Hz), 7.43 (d, 2H, J = 5.4 Hz), 7.29 (t, 6H, J = 7.8), 7.06 (t, 8H, J = 7.8 Hz), 6.99 (d, 2H, J = 5.9 Hz), 6.76 (q, 7H, J = 5.3 Hz), 6.54 (s, 2H), 2.46 (t, 4H, J = 7.8 Hz), 1.32 (m, 4H), 1.11 (m, 4H), 1.02 (m, 8H), 0.75 (t, 6H, J = 7.0 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz)  $\delta$  10.1 (s), -147 (sept, J = 705 ppm). ESI-MS: m/z 1428 ([M-PF<sub>6</sub>]<sup>+</sup>). Anal. Calcd for C<sub>71</sub>H<sub>65</sub>F<sub>12</sub>N<sub>3</sub>P<sub>4</sub>RuS<sub>5</sub>: C, 54.19; H, 4.16; N, 2.67. Found: C, 53.79; H, 4.24; N, 2.71.

#### X-Ray Crystallography

All crystals were mounted on glass fibers. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K $\alpha$  radiation. Data were collected and integrated using the Bruker SAINT<sup>37</sup> software package. Data were corrected for absorption effects using the multi-scan technique (SADABS).<sup>38</sup> The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods.<sup>39</sup>

**2.DMF.** The data were collected to a maximum  $2\theta$  value of 47.8°. Data were collected in a series of  $\phi$  and  $\omega$  scans in 0.50° oscillations with 15.0 second exposures. The crystal-todetector distance was 36.00 mm. Of the 28819 reflections that were collected, 11495 were unique ( $R_{int} = 0.034$ ); equivalent reflections were merged. The minimum and maximum transmission coefficients were 0.791 and 0.952, respectively. The material crystallizes with two independent Ru complexes in the asymmetric unit. Additionally there are two molecules of DMF in the asymmetric unit. One DMF molecule was disordered and was modeled in two orientations. All non-hydrogen atoms except those in the disordered DMF molecule were refined anisotropically. All hydrogen atoms were placed in calculated positions but were not refined. The material also crystallizes as a racemic twin. The SHELXL TWIN/BASF functions were used to model the ratio of twin components accordingly. The final cycle of full-matrix leastsquares refinement on  $F^2$  was based on 11495 reflections and 931 variable parameters and converged.

7. The data were collected to a maximum  $2\theta$  value of 55.9°. Data were collected in a series of  $\phi$  and  $\omega$  scans in 0.50° oscillations with 10.0-second exposures. The crystal-to-detector distance was 36.00 mm. Of the 76558 reflections that were collected, 20031 were unique ( $R_{int} = 0.043$ ); equivalent reflections were merged. Data were corrected for absorption effects with minimum and maximum transmission coefficients of 0.898 and 0.950, respectively. The material crystallizes with two independent molecules in the asymmetric unit. There is a small fraction of disorder regarding the orientation of the terthiophene moiety in each molecule. This disorder was modeled using restraints on bond lengths and angles

such that the minor fragments had geometries similar to those of the major fragments. All non-hydrogen atoms in the major fragments were refined anisotropically. All hydrogen atoms were placed in calculated positions but were not refined. The final cycle of full-matrix least-squares refinement on  $F^2$  was based on 20031 reflections and 1244 variable parameters, and converged.

 $8 \cdot 0.63 H_2 O$ . The data were collected to a maximum  $2\theta$  value of 56.1°. Data were collected in a series of  $\phi$  and  $\omega$  scans in 0.50° oscillations with 20.0 second exposures. Of the 105257 reflections that were collected, 12056 were unique ( $R_{int} = 0.072$ ); equivalent reflections were merged. Data were corrected for absorption effects with minimum and maximum transmission coefficients of 0.798 and 0.937, respectively. All non-hydrogen atoms were refined anisotropically. Two phenyl rings on P1 are disordered and were each modeled in two orientations. Additionally, one PF<sub>6</sub>anion is disordered, with all six fluorine atoms modeled in two orientations. Restraints were employed to maintain reasonable octahedral geometry about the P atom. Finally, a water molecule is found at one site in the asymmetric unit. This site is only partially occupied (the relative population is 0.63) and no hydrogen atoms could be located in a difference map. All hydrogen atoms were placed in calculated positions. The final formula and values derived from it are based on the presence of 0.63 molecules of  $H_2O$ . The final cycle of full-matrix least-squares refinement on  $F^2$  was based on 12056 reflections and 790 variable parameters and converged.

#### **Results and Discussion**

#### Synthesis and Structures

The orange complex 1 was synthesized by combining  $P_2T_3$  and  $Ru(DMSO)_4Cl_2$  in toluene and heating the mixture to reflux (Scheme 2).<sup>40</sup> <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra are consistent with tridentate binding of  $P_2T_3$  to the metal centre. The IR spectrum of 1 has a v(S=O) absorption band at 1009 cm<sup>-1</sup>, indicating that the DMSO is O-bound.<sup>41</sup> The steric bulk of  $P_2T_3$  on Ru(II) may make the formation of a Ru–S bond with DMSO unfavorable.



Increased  $\pi$  conjugation in thiophene oligomers typically results in an increase in the molar absorptivity and a lowering of the oxidation potential, both of which can be beneficial for light-harvesting applications and in facilitating electropolymerizability. To extend the  $\pi$ -conjugation of P<sub>2</sub>T<sub>3</sub>, the pentamer P<sub>2</sub>T<sub>5</sub> was prepared (Scheme 3). Iodination of both  $\alpha$ -positions of Br<sub>2</sub>T<sub>3</sub> with NIS, gave I<sub>2</sub>Br<sub>2</sub>T<sub>3</sub>. This was followed by Suzuki coupling of I<sub>2</sub>Br<sub>2</sub>T<sub>3</sub> with 2-(3-hexyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane<sup>33</sup> to



Scheme 3

give  $Br_2T_5$ . Lithiation of  $Br_2T_5$ , followed by reaction with PPh<sub>2</sub>Cl formed  $P_2T_5$ .<sup>31</sup>

Complex 5 was prepared by heating Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> and P<sub>2</sub>T<sub>5</sub> in toluene to reflux (Scheme 1). The hexyl side chains on the pentathiophene resulted in 5 being soluble in toluene. The DMSO is also O-bound in 5, as evident from the v(S=O) band at 1015 cm<sup>-1</sup> in the IR spectrum.

The DMSO complexes 1 and 5 provide a starting point for preparing other complexes containing the  $Ru(P_2T_3)$  or  $Ru(P_2T_3)$ core. Ligand displacement was straightforward, but sensitive to solvent. To exchange DMSO for CH<sub>3</sub>CN, 1 was dissolved in a hot mixture of DMF and CH<sub>3</sub>CN, diethyl ether was added and the mixture cooled to yield 2. The CH<sub>3</sub>CN complex 2, in turn, can be used as a starting material to prepare 3 by adding 4,4'byy in hot acetone. Quaternatization of the free pyridine in 3 was accomplished by a solvent free synthesis in which a mixture of 2 and [*N*-Me-4,4'-bpy]I was heated to give 4 (Scheme 4).



The geometry around Ru(II) in complexes 1–5 can be either *cis* or *trans* with respect to the chloro groups. Far IR spectra have been used to differentiate between cis- and trans-isomers of complexes containing the RuCl<sub>2</sub> unit by determining the number of Ru–Cl bands present, but in this case the Ru–S and Ru–P bands overlap with the Ru–Cl bands. Analysis of the far IR spectra of the dichloro-Ru(P<sub>2</sub>T<sub>3</sub>) complexes was thus inconclusive as to whether cis, trans, or mixtures of isomers were obtained. In cases where crystal structures were not obtained, the complexes are all arbitrarily shown in the Schemes as the cis-isomers. Their purification was considered complete when only one peak was observed in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. The specific isomers

obtained in dichloro-Ru(II) complexes are known to depend on the ligands around Ru(II), solvent and temperature.<sup>42</sup>

Single crystals of 2 were grown from a DMF/CH<sub>3</sub>CN/Et<sub>2</sub>O solution, and the solid state structure is shown in Fig. 1. In the solid state, there are two, crystallographically unique, molecules of 2 each with bond lengths and angles within experimental error of the other (Table S2 and S3<sup> $\dagger$ </sup>). P<sub>2</sub>T<sub>3</sub> binds as a tridentate ligand to Ru(II), with two six-membered rings containing the Ru(II) centre, as observed in other phosphino-oligothienvl-Ru(II) complexes bonded through the thiophene sulfur.<sup>28,29</sup> The torsion angles between the two pairs of adjacent thiophene rings are similar  $(154.4(3)^{\circ} \text{ and } -153.2(3)^{\circ})$ . This results in pseudo-C<sub>s</sub> symmetry in 2 at the metal centre (neglecting the phenyl rings of the aryl phosphines). The Ru–S bond length is 2.2486(12) Å, significantly shorter than observed in a similar RuCl<sub>2</sub>-phosphinooligothiophene which has a Ru-S bond length of 2.3068(9) Å.43 **2** DMF packs with a series of slipped  $\pi$ -interactions between S1 and S2 thiophenes and S3 and S6 thiophenes (between the crystallographically unique complexes).



**Fig. 1** Solid-state molecular structure of one molecule of **2**·DMF. Occluded DMF and H atoms omitted for clarity. Thermal ellipsoids drawn at 50% probability.

The number of chloro ligands coordinated to the Ru centre affects the charge on the Ru and hence the electronic structure of the Ru. Therefore, it was of interest to prepare cationic Ru complexes by abstracting one of the Cl ligands. Four such cationic complexes (6–9) were prepared. Complexes 7–9 each have only one possible isomer which allows more conclusive structural characterization. The synthesis of all four complexes was accomplished by dehalogenation with AgBF<sub>4</sub>. Complexes 8 and 9 were synthesized *via* dehalogenation of Ru(tpy)Cl<sub>2</sub>(DMSO) in MeOH prior to addition of P<sub>2</sub>T<sub>3</sub> and P<sub>2</sub>T<sub>5</sub>, respectively (Scheme 5).



Single crystals of **8** were grown from a hexanes/acetone solution and the solid state molecular structure is shown in Fig. 2. Disorder was present in two of the phenyl rings and in one of the  $PF_6^$ anions. The  $P_2T_3$  ligand is coordinated in a tridentate fashion, as in **2**, and the molecule has pseudo- $C_s$  symmetry (neglecting the



**Fig. 2** Solid-state molecular structure of 8.0.63  $H_2O$ . H atoms, occluded solvent and  $[PF_6]^-$  counterions omitted for clarity.

phenyl rings of the aryl phosphines). The two interannular torsion angles in the terthiophene are similar  $(141.1(3)^{\circ} \text{ and } -144.6(3)^{\circ})$  and comparable to the torsion angles in **2**. Complex **8** has a Ru–S bond length of 2.3309(12) Å, the longest of the three Ru(II) complexes that have been structurally characterized. This bond length is still shorter than in other related phosphino-thienyl-Ru(II)-polypyridine complexes.<sup>29</sup>

Complexes 6 and 7 were prepared by reacting the appropriate Ru(II) starting material directly with  $P_2T_3$  in one step, in CHCl<sub>3</sub> and CH<sub>3</sub>CN solutions, respectively (Scheme 6). Despite the presence of excess  $P_2T_3$  and AgBF<sub>4</sub> in the synthesis of 6, there was no evidence for formation of complexes containing more than one  $P_2T_3$  ligand, such as  $[Ru(P_2T_3)_2][PF_6]_2$ . It is possible that the steric bulk of  $P_2T_3$  prevented further dehalogenation of the Ru(II) centre. The IR spectrum of 6 contained only one band attributable to v(C=N), suggesting a high symmetry species formed. The <sup>1</sup>H NMR spectrum of 6 contained one singlet at  $\delta$  2.77 ppm, indicating that the –CH<sub>3</sub> groups of the coordinated CH<sub>3</sub>CN are chemically equivalent in solution, hence, 6 is proposed to be the *trans* isomer.



Single crystals of 7 were obtained from acetone/MeOH/hexanes solution and the solid-state structure of one of the molecules in the unit cell is shown in Fig. 3. There are two crystallographically unique molecules with similar bond lengths and angles in the unit cell (Table S4 and S5†). The two internannular torsion angles between the thiophene rings  $(172.0(2)^{\circ}$  and  $133.8(3)^{\circ})$  are significantly different in this



Fig. 3 Solid-state molecular structure of one of the two molecules of 7 in the unit cell. H atoms and  $[PF_6]^-$  counterion omitted for clarity and thermal ellipsoids drawn at 50% probability.

Table 1 Electronic absorption data for complexes 1-9

Complex	$\lambda_{\rm max}/{\rm nm} \left(\epsilon/{\rm M}^{-1}{\rm cm}^{-1}\right)$
1	268 (28 000), 395 (11 000), 446 (sh) (4 000) <sup>a</sup>
5	$265(34\ 000), 414(17\ 000)^a$
2	260 (42 000), 392 (15 000), 448 (sh) (3000) <sup>a</sup>
3	260 (45 000), 393 (15 000), 450 (sh) (3300) <sup>a</sup>
4	257 (45 000), 387 (11 000), 447 (sh) (3000) <sup>a</sup>
6	260 (43 000), 384 (14 000), 434 (sh) (3300) <sup>b</sup>
7	259 (39 000), 300 (sh) (16 000), 378 (14 000), 416 (sh) (9300) <sup>b</sup>
8	259 (41 000), 296 (sh) (24 000), 333 (18 000), 387 (15 000) <sup>b</sup>
9	$263 (49\ 000), 297 (37\ 000), 333 (25\ 000), 445 (30\ 000)^{b}$
<sup>a</sup> In CH <sub>2</sub> Cl	<sup>b</sup> In CH <sub>2</sub> CN.

structure. The Ru–S distance is 2.282(9) Å, lengthened compared to the Ru–S distance in **2**. This is still shorter than in similar Ru-polypyridine systems where the bond lengths are 2.3578(14) Å<sup>29</sup> and 2.3640(8) Å.<sup>29</sup>

#### **Electronic Absorption Spectra**

The UV-vis absorption spectra for the series of Ru(II) complexes are shown in Fig. 4 and the data summarized in Table 1. The absorption spectra are dominated by  $\pi$ -based transitions. All of the complexes have a  $\pi \rightarrow \pi^*$  transition at 260 nm which is slightly red-shifted from the  $\pi \rightarrow \pi^*$  band in P<sub>2</sub>T<sub>3</sub> (253 nm). Remarkably, between 350–550 nm there is little difference in the spectra of the seven complexes containing the P<sub>2</sub>T<sub>3</sub> ligand (1–4, 6–8).

The absorption spectra of complexes 1–4 each have a strong band at ~390 nm. This absorption band is bathochromically shifted with respect to the lowest energy band of  $P_2T_3$  ( $\lambda_{max}$  = 360 nm). Similar Ru(II)-oligothiophene complexes have  $\pi$ -based transitions on the terthiophene red-shifted from the comparable absorbance band of the oligothiophene.<sup>43</sup> This bathochromic shift is attributed to the Ru centre donating electron density to the terthiophene and the increased rigidity of the oligothiophene as a result of coordination to the metal,<sup>43</sup> and a similar effect is likely involved in the electronic spectra of the Ru(II) complexes studied here.

The lowest energy bands in complexes 6-8 are hypsochromically shifted from the comparable bands in complexes 1-4, however the similarity in the absorption maxima of 6-8 to



Fig. 4 Solution absorption spectra of (a) 1-5 in CH<sub>2</sub>Cl<sub>2</sub> and (b) 6-9 in CH<sub>3</sub>CN.

complexes 1–4 suggests that these transitions also have  $\pi$ character. MLCT transitions were observed in previously studied Ru(II) bipyridyl complexes with oligothiophene ligands.<sup>29</sup> Both 7 and 8 also have chelating polypyridines, so it is possible that there is a MLCT component in addition to a  $\pi \rightarrow \pi^*$  component for the lowest energy band. To elucidate whether MLCT transitions partially contributed to the observed bands, the electronic absorption spectra were recorded in solvents of different polarity (toluene, CH<sub>2</sub>Cl<sub>2</sub>, MeOH, THF and acetonitrile where possible). The lowest energy band of 8 shifted from 408 nm in toluene to 386 nm in THF, which suggests that this band may indeed have some charge transfer character. In 7, the band at 378 nm was solvent independent, whereas the shoulder shifted from 412 nm in THF to 423 nm in toluene. The solvent sensitivity of the shoulder suggests that MLCT contributions are responsible for this band. All of the other complexes had solvent independent bands. Complexes 7 and 8 had additional bands between 280 nm-350 nm. The bands at 296 nm and 333 nm in 8 are red-shifted from those of  $[Ru(tpy)_2]^{2+}$  ( $\lambda_{max} = 269$  and 308 nm), similar to the shifts seen in  $[Ru(tpy)(pydppz)]^{2+}$  (pydppz = 3-(pyrid-2'-yl)dipyrido[3,2-yl)dia: 2,3'-c] phenazine)<sup>44</sup> and  $[Ru(tpy)(tripy)]^{2+}$  (tripy = 2,6-bis(1H-1,2,3-triazol-4-yl)pyridine).<sup>45</sup> Likewise, the transitions in 7 are similar to those in *cis*-Ru(2,2'-bpy)<sub>2</sub>Cl<sub>2</sub><sup>46</sup> ( $\lambda_{max} = 340$  nm, 400–500 nm (MLCT)), [Ru(2,2'-bpy)(tpy)Cl]<sup>+</sup>,<sup>47</sup> ( $\lambda_{max} = 292$  nm, 316 nm, 501 nm (MLCT)) and [Ru(PT<sub>3</sub>-P,S)(2,2'-bpy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>.<sup>29</sup>

Extending the conjugation in the ligand led to a bathochromic shift in the lowest energy absorption band for **5** and **9** compared to the complexes containing  $P_2T_3$ . This large shift in the lowest energy band suggests that it is dominated by ligand-based  $\pi \rightarrow \pi^*$  transitions on  $P_2T_5$ . Furthermore, the bands were all solvent-independent, which is consistent with  $\pi \rightarrow \pi^*$  character. The higher energy bands for **5** and **9** are identical to those in **1** and **8**, suggesting that these transitions are not localized on the oligothiophene.

Low temperature absorption spectra of the complexes were also obtained for further insight into the electronic structure of the complexes (see ESI<sup>†</sup>). None of the complexes show shifts in their absorbance bands when cooled to 85 K from room temperature. This suggests that there is no significant change in planarity of the terthienyl groups over this temperature range. Cooling enhances the vibronic coupling in most of the complexes, consistent with the presence of a delocalized electronic system. In 1–5 the lowest energy band at ~390 nm separates into 2 bands at 85 K. In 1 and 2 the lowest energy bands separate by ~1100 cm<sup>-1</sup>, while the comparable bands in 3 and 4 separate by 960 cm<sup>-1</sup>. These separations are typical of vibrational coupling with the thienyl groups.<sup>48,49</sup> Alternatively, it is possible that these bands are due to *cis* and *trans* isomers. Different isomers can have different absorbance bands as seen in related Ru(II)-thienyl *cis* and *trans* isomers where  $\pi$ – $\pi$ \* absorption bands were separated by 560 cm<sup>-1</sup>.<sup>43</sup> Lengthening the ligand conjugation in 5 results in notable changes in the low temperature absorption features where the lowest energy band separated into two bands separated by ~2300 cm<sup>-1</sup>. The large energy difference between the bands in 5 suggests that two different electronic states, rather than vibrational coupling, may be responsible for the two bands.

The spectra of complexes **6–9** show similar features to complexes **1–5** at low temperature. The band at 385 nm in **6** separates into two bands with a ~1000 cm<sup>-1</sup> difference at 85 K. The shoulder at 423 nm for **7** becomes more resolved at 85 K. In both **7** and **8** the single band at 385 nm at room temperature, has two shoulders at 85 K separated by ~1200 cm<sup>-1</sup>. This energy difference is consistent with either thienyl or polypyridyl vibrational coupling.<sup>48-50</sup> Extending the conjugation in the cationic complexes in **9** afforded similar results, where the lowest energy band had vibrational shoulders separated by ~1100 cm<sup>-1</sup>.

None of the complexes were emissive at either room temperature or 85 K.

To further investigate the electronic structure of 7, time-resolved transient absorption (TA) spectra were obtained in CH<sub>3</sub>CN solution (Fig. 5). This complex was selected for study by TA due to its easy purification and solubility in CH<sub>3</sub>CN. Excitation at 355 nm resulted in a TA band at 475 nm. No bleach is observed in the spectral range examined and the ground state absorption before and after transient absorption was identical, indicating photo-decomposition was negligible during the experiment. [Ru(2,2'-byy)<sub>3</sub>]<sup>2+</sup> has a transient absorption band at 360 nm attributed to a transition on the reduced 2,2'-bpy<sup>51</sup> while the triplet state in terthiophene is observed at 450 nm<sup>52</sup> and oxidized terthiophene at 545 nm.<sup>53</sup> The lifetime of the 475 nm transient absorption band in 7 is 108 ± 1 ns in aerated CH<sub>3</sub>CN (Fig. 5) and 171 ± 8 ns in deaerated CH<sub>3</sub>CN, which is shorter than expected for a ligand-based triplet species, but typical of a charge transfer state such as



Fig. 5 Time resolved transient absorption spectra of 7 in  $CH_3CN_2$ 

in [Ru(2,2'-bpy)(tpy)Cl]<sup>+</sup> which has an emission lifetime of 110 ns in CH<sub>3</sub>CN<sup>54</sup> and Ru(dcbpy)<sub>2</sub>(SCN)<sub>2</sub> (dcbpy = 4,4'-dicarboxyl-2,2'bipyridyl) which has an emission lifetime of 50 ns.<sup>55</sup> It is difficult to unambiguously assign the species observed in the TA, however, the energy of the TA band and increase in lifetime in the absence of  $O_{2(g)}$  is most consistent with a terthiophene localized triplet state. The presence of the Ru could be providing alternate decay pathways that result in a short triplet lifetime.

#### Cyclic Voltammetry

The ligand influence on the electrochemical oxidation potentials of Ru(II) complexes has been correlated to the observed Ru(II/III) oxidation potential ( $E_{obs}$ ) for several common ligands, to give a ligand electrochemical parameter ( $E_L$ ) (in V vs NHE).<sup>56</sup> The observed oxidation potential is given by:  $E_{obs} = 0.97[\Sigma E_L] + 0.04.^{56}$  $E_L$  values have been determined for several of the ligands in the Ru(II) complexes described here; specifically Cl<sup>-</sup> (-0.24 V), DMSO (0.47 V), CH<sub>3</sub>CN (0.34 V), 4,4'-bpy (0.27 V), 2,2'-bpy (0.259 V) and tpy (0.25 V).<sup>56</sup>

Complexes 1–4 and 6–8 have  $P_2T_3$  bound to the Ru(II) centre in a tridentate manner, thus  $E_L$  can be determined for  $P_2T_3$  $(E_{P_2T_3})$  using oxidation potential data for the series of complexes. Whether  $E_{P_2T_3}$  depends on the Ru-thiophene bond length or Ruthiophene angle, both known to influence metal-thienyl  $\pi$ -backbonding,<sup>57</sup> is of interest. The cyclic voltammograms (CVs) of the complexes were obtained in CH<sub>2</sub>Cl<sub>2</sub>, and the oxidation potential data collected in Table 2.

The Ru(II/III) oxidation potentials for complexes 1–4 are consistent with the trend predicted from the  $E_{\rm L}$  values of CH<sub>3</sub>CN, DMSO, and 4,4'-bpy.<sup>56</sup> An oxidation wave for the P<sub>2</sub>T<sub>3</sub> ligand was not observed in any of complexes 1–4. Increasing the ligand conjugation length in 5 resulted in a decrease in the oxidation potential of the oligothiophene, with an oxidation wave at 1.48 V. The cationic complexes 6–9 had Ru(II/III) oxidation waves anodically shifted from those for complexes 1–4, as predicted by the larger  $E_{\rm L}$  values of the ancillary ligands. The Ru(II/III) oxidation since they occurred at similar potentials in these complexes. Complexes 6–8 all have an irreversible oxidation wave at ~1.7 V which suggested a common moiety was oxidized at this potential. From this, it was concluded that the common oxidation waves at 1.24 V, 1.93 V, and 2.08

Table 2	Oxidation and	reduction	potentials	of complexes 1-9
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Compound	Ru(II/III)/V vs. SCE ( $\Delta E/mV$ )	Ligand/V vs. SCE	$E_{P_2T_3}/V$ vs. NHE	$\frac{E_{1/2, \text{ red}}/\text{V } vs}{\text{SCE} (\Delta E/\text{mV})}$
1 <sup>b</sup>	1 17 <sup>c</sup>	_	1.42	
$2^b$	0.77 (45)		1.12	
3 <sup>b</sup>	1.08 (70)		1.53	
<b>4</b> <sup>b</sup>	1.29 <sup>c</sup>		N/A	
5 <sup><i>b</i></sup>	$1.19^{c}$	$1.48^{c}$	1.46	
<b>6</b> <sup><i>a</i></sup>	$2.08^{c}$	$1.72^{c}$	1.91	$1.49^{c} (P_{2}T_{3}^{0/-})$
<b>7</b> <sup>a</sup>	1.24°	1.76 <sup>c</sup>	1.46	$-1.38^{\circ}(P_2T_3^{0/-}),$ -1.57 (110) (2.2'-bpy^{0/-})
<b>8</b> <sup><i>a</i></sup>	1.93 <sup>c</sup>	1.73 <sup>e</sup>	1.95	$-1.35^{\circ}$ (P <sub>2</sub> T <sub>3</sub> <sup>0/-</sup> ), -1.67 (100) (tpv <sup>0/-</sup> )
<b>9</b> <sup>a</sup>	N/A	1.20, 1.28		_
$P_2T_3^{b}$	N/A	$1.40,^{c}$ $1.65^{c}$		
$P_2T_5^{b}$	N/A	$0.72,^{c}$ $1.56^{c}$		

<sup>*a*</sup> Recorded in CH<sub>3</sub>CN with 0.1 M [*n*-Bu<sub>4</sub>N][PF<sub>6</sub>]. <sup>*b*</sup> Recorded in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M [*n*-Bu<sub>4</sub>N][PF<sub>6</sub>]. <sup>*c*</sup> Irreversible oxidation wave,  $E_p$ .

V are due to the Ru(II/III) oxidation for 7, 8 and 6 respectively. Hence coordination of Ru to  $P_2T_3$  causes a positive shift of the  $P_2T_3$  oxidation wave.

The Ru(II/III) oxidation potentials varied between 0.77 V to 2.08 V for all the complexes.  $E_{P_2T_3}$  was calculated where possible using this data, and a value that varied between 1.15 V to 1.95 V was obtained. In order to determine whether this difference could be related to the Ru–S bond length,  $E_{P_2T_3}$  vs the Ru–S bond length was plotted for complexes **2**, **7** and **8** (see ESI†). A linear relationship was obtained between the Ru–S bond length and  $E_{P_2T_3}$ , however no correlation was found between the Ru–thiophene angle and  $E_{P_2T_3}$ . Thus, the proximity of the central thiophene to the Ru centre dramatically influences the observed Ru(II) oxidation potential. The closer the thienyl sulfur is to the metal centre, the lower the oxidation potential of the Ru(II) centre.

Complex 7 has two reduction waves; an irreversible wave at -1.38 V and a quasi-reversible wave at -1.57 V. Similarly, 8 also has two reduction waves; an irreversible wave at -1.35 V and a quasireversible wave at -1.67 V. Complex 6 has a single irreversible reduction wave at -1.49 V. To probe the nature of the reduction waves, the difference between the ligand oxidation potential and the irreversible reduction waves of 6-8 was calculated. The calculated differences were between 3.08 eV (403 nm) to 3.21 eV (386 nm). This value is similar to the energy of the  $\pi \rightarrow \pi^*$  transition in the absorption spectra of the complexes, so the irreversible reduction wave may be due to reduction of the terthiophene backbone of  $P_2T_3$ . The quasi-reversible waves of 7 and 8 are assigned to reduction of the polypyridine ligands. A similar Ru(II)bipyridyl-oligothiophene complex has a reduction wave at -1.28 V vs SCE,<sup>29</sup> [Ru(bpy)<sub>3</sub>]<sup>2+</sup> has a reduction wave at -1.36 V vs SCE<sup>58</sup>  $([Ru(bpy)_3]^{2+}$  is also reported to have two reduction waves at -1.73 V and -1.98 V vs ferrocene<sup>59</sup>) and [Ru(tpy)<sub>2</sub>]<sup>2+</sup> has reduction waves at -1.66 V and -1.96 V vs ferrocene.59

None of the complexes electrochemically polymerized under the conditions employed for the cyclic voltammetry. It is possible that the steric bulk imposed by the diphenylphosphine groups prevents the complexes from oxidatively coupling at the terminal  $\alpha$ -positions of the P<sub>2</sub>T<sub>3</sub> backbone. Using P<sub>2</sub>T<sub>5</sub> rather than P<sub>2</sub>T<sub>3</sub>

should decrease the steric bulk near the  $\alpha$ -position of the terminal thiophenes and result in a decrease in the oxidation potential of the oligothiophene, which could encourage electrochemical polymerization. The pentathiophene complexes 5 and 9 both had oligothiophene oxidation waves at lower potentials than those in the analogous terthiophene complexes 1 and 8, but even in these complexes no conducting material was deposited on the electrode with repeated cycling. The lack of electropolymerization could be a result of the spin density not being localized on the terminal  $\alpha$ -position of the oligothiophene upon oxidation.

#### Five-Coordinate Ru(II) Species

When complexes 1 or 2 were dissolved in non-coordinating or weakly coordinating solvents such as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, THF or DMF, they changed from orange to green in colour. Complex 1 immediately began changing colour in CH<sub>2</sub>Cl<sub>2</sub>, whereas 2 gradually changed colour overnight. Both species showed a new absorption band at 729 nm in CH<sub>2</sub>Cl<sub>2</sub> (Fig. 6). Similarly, 5 shows a band that appears at 729 nm in CH<sub>2</sub>Cl<sub>2</sub>. None of the cationic complexes showed a dramatic colour change in any solvent.



Fig. 6 Absorbance spectra of 1 and 2 after being dissolved in  $CH_2Cl_2$ overnight.

To elucidate the species responsible for the colour change, the absorption and NMR spectra of 1, in CH<sub>2</sub>Cl<sub>2</sub> and CDCl<sub>3</sub> solutions respectively, were monitored over several hours. The absorption band at 729 nm increased in intensity at a rate of ~0.006 min<sup>-1</sup>. The peak in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at  $\delta$  1.54 ppm in CDCl<sub>3</sub> disappeared over several hours as the solution became green. No new peaks were observed and no broadening was apparent in the baseline during this experiment. Likewise, the <sup>1</sup>H NMR spectra in CDCl<sub>3</sub> did not show any peak broadening with time, which suggests that a diamagnetic species is responsible for the colour change. The aromatic region of the <sup>1</sup>H NMR spectra became increasingly complicated with time, and the peak due to coordinated DMSO at  $\delta$  1.79 ppm decreased in intensity over time. Concurrently, the peak due to free DMSO at  $\delta$  2.62 ppm increased in relative intensity (see ESI<sup>†</sup>). The changes in the NMR peak intensities occurred at a rate of ~0.004 min<sup>-1</sup>, approximately the same as the rate of appearance of the 729 nm band in the absorption spectrum.

Together the electronic absorption and <sup>1</sup>H NMR spectra suggest that the DMSO coordinated to the Ru(II) dissociates to give a green 5-coordinate species, putatively Ru(P<sub>2</sub>T<sub>3</sub>)Cl<sub>2</sub>, in non-coordinating

solvents. Other five-coordinate Ru(II) complexes are also green, for example,  $Ru(dpb)Cl_2$  (dpb = 1,4-bis(diphenylphosphino)butane) is pale green<sup>60</sup> and RuCl<sub>2</sub>(HPNP<sup>tBu</sup>) (HPNP<sup>tBu</sup> = HN(CH<sub>2</sub>CH<sub>2</sub>P(t- $(Bu_2)_2$ ) is turquoise.<sup>61</sup> Ru(II) complexes are well known to undergo dissociative reactions.<sup>62</sup> When a green CH<sub>2</sub>Cl<sub>2</sub> solution of 1 was evaporated and the residue dissolved in DMSO overnight, the solution changed from green to orange in colour. This is consistent with the green  $Ru(P_2T_3)Cl_2$  coordinating DMSO resulting in reformation of orange 1.

### Conclusions

A series of Ru(II) complexes containing the conjugated oligothiophene ligands  $P_2T_3$  and  $P_2T_5$  were prepared and characterized. The crystal structures obtained show that P2T3 bonds as a tridentate ligand to Ru(II). Interestingly, complexes 1, 2 and 5 all showed a band at 729 nm when left dissolved in non-coordinating solvents. This green colour is attributed to the formation of a five-coordinate Ru(II) complex in solution. The cationic complexes, by contrast, were stable for at least two days in non-coordinating solvents. The cyclic voltammograms of all the complexes were obtained. For the  $P_2T_3$  complexes,  $E_{P_3T_3}$  was determined and found to depend on the Ru-S bond length. The increased conjugation in 5 and 9 resulted in a lowering of the oxidation potential of the oligothiophene, but this did not enable electropolymerization of a Ru(II) complex.

The electronic spectra were dominated by  $\pi \rightarrow \pi^*$  transitions, and complexes 7 and 8 also had charge transfer bands. At low temperature, the electronic spectra of a number of the complexes resolved into two bands, either due to vibronic coupling or resolution of isomer bands. Similarly, the spectra of complexes 7-9 had shoulders that resolved at 85 K typical of vibronic coupling with oligothiophenes or polypyridines. All of the Ru(II) complexes were non-emissive at room temperature and low temperature, indicating the excited state decays by other, non-radiative pathways. The transient absorption spectrum of complex 7 has a band at 475 nm which was most consistent with a ligand (terthiophene) localized triplet state. The species has a lifetime of ~100 ns, consistent with this assignment. Application of these complexes as dyes in solar cells will require tuning the MLCT and ligand triplet energies to allow population of the MLCT state and injection of electrons into the conduction band of TiO<sub>2</sub>. Recent work by Schmehl has demonstrated that Ru complexes with ligandlocalized triplet states can undergo excited state electron transfer reactions involving the metal.<sup>63</sup> This observation suggests that complexes such as those synthesized here could be useful in dyesensitized solar cells provided a carboxylic acid tether is appended to allow surface functionalization of TiO<sub>2</sub>.

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